

PB-220 077

Regeneration Chemistry of Sodium-Based Double-Alkali Scrubbing Process

National Environmental Research Center

prepared for

Office of Research and Monitoring

MARCH 1973

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U. S. DEPARTMENT OF COMMERCE**

EPA-R2-73-186

March 1973

PB 220 077

Environmental Protection Technology Series

Regeneration Chemistry of Sodium-Based Double-Alkali Scrubbing Process



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U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711**

BIBLIOGRAPHIC DATA SHEET		1. Report No. EPA-R2-73-186	2.	3. Recipient's Accession No. 18-220 977
4. Title and Subtitle Regeneration Chemistry of Sodium-Based Double-Alkali Scrubbing Process			5. Report Date March 1973	6.
7. Author(s) Dean C. Draemel			8. Performing Organization Rept. No.	
9. Performing Organization Name and Address EPA, Office of Research and Monitoring NERC/RTP, Control Systems Laboratory Research Triangle Park, North Carolina 27711			10. Project/Task/Work Unit No. 21 ACX 38	
			11. Contract/Grant No. NA	
12. Sponsoring Organization Name and Address EPA, Office of Research and Monitoring Washington, D. C. 20460			13. Type of Report & Period Covered Final	
			14.	
15. Supplementary Notes				
16. Abstracts The report gives the results of a study of the reactions of calcium hydroxide, calcium carbonate, and limestone with the aqueous (sodium, sulfite, bisulfite, and sulfate) system. Concentrations and stoichiometries typical of those for sodium-based double-alkali scrubbing systems were used. The reactions were studied in a stirred, nitrogen-purged glass reaction vessel immersed in a constant-temperature bath. The objectives were to study various reactions of importance in the sodium-based double-alkali process and to define possible operating modes for the process. Results indicate desirable operating ranges and may be used to support engineering design of pilot-scale double-alkali scrubber systems. Appendices include experimental data, references, and theoretical discussions.				
17. Key Words and Document Analysis. 17a. Descriptors Air Pollution *Desulfurization Flue Gases Washing Chemical Reactions Sodium Inorganic Compounds Alkalis Regeneration (Engineering) Limestone Sulfur Compounds Reaction Kinetics				
17b. Identifiers/Open-Ended Terms Air Pollution Control Stationary Sources *Double-Alkali Process Sodium/Calcium Process Throwaway Process				
17c. COSATI Field/Group 13B				
18. Availability Statement Unlimited			19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 48 37
			20. Security Class (This Page) UNCLASSIFIED	22. Price \$3 75

Regeneration Chemistry of Sodium-Based Double-Alkali Scrubbing Process

by

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Program Element No. 1A2013

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Prepared for

OFFICE OF RESEARCH AND MONITORING
NATIONAL ENVIRONMENTAL RESEARCH CENTER
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711

March 1973

ABSTRACT

Reactions of Ca(OH)_2 , CaCO_3 , and limestone with the aqueous (Na^+ , SO_3^- , HSO_3^- , SO_4^{2-}) system were studied. Concentrations and stoichiometries typical of those for sodium-based double-alkali scrubbing systems were used. The reactions were studied in a stirred, nitrogen-purged glass reaction vessel immersed in a constant-temperature bath. The objectives were to study various reactions of importance in the sodium-based double-alkali process and to define possible operating modes for the process.

Results indicate desirable operating ranges and may be used to support engineering design of pilot-scale double-alkali scrubber systems.

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SECTION I

CONCLUSIONS

1. The reactions between CaCO_3 or limestone and the Na^+ , SO_3^{2-} , HSO_3^- , SO_4^{2-} system are dependent on HSO_3^- and SO_3^{2-} concentration, SO_4^{2-} concentration (ionic strength), CaCO_3 particle size, and agitation level. Other factors have lesser effects.

2. Bisulfite neutralization with CaCO_3 or limestone requires roughly 2 hours for 90 percent of the reaction to occur. CaCO_3 utilization ranged from 90-40 percent with stoichiometry 1.0 and from 66-40% with stoichiometry 1.5, both at a total initial sulfite ($\text{HSO}_3^- + \text{SO}_3^{2-}$) level of 0.088M. In general, higher bisulfite concentrations (0.055M vs 0.022M) are neutralized more rapidly, providing better utilization of CaCO_3 or limestone. Increasing sulfate levels appears to suppress

bisulfite neutralization as indicated by the range of CaCO_3 utilizations.

3. Lime reacts with sulfate in the presence of limited sulfite up to an equilibrium hydroxide level of roughly 0.14M OH^- (Appendix C). The reaction with sulfite is suppressed at higher sulfate levels. The decrease in the extent of the reaction between lime and sulfite with increasing sulfate implies that sulfate regeneration is possible even in the presence of sulfite ion concentrations in excess of that necessary to produce $\sim 0.14\text{M}$ hydroxide ion concentrations.

4. Higher sulfate levels appear to suppress both the neutralization of bisulfite and the precipitation of sulfite with limestone or lime.

SECTION II

RECOMMENDATIONS

On the basis of batch test results and similar studies done by other organizations, a continued effort to characterize the double-alkali system and to develop it through a pilot plant or small-scale demonstration is suggested. The proposed double-alkali program should be carried on as planned.

Additional batch tests should be conducted

to define ranges of possible operation to help define oxidation effects in the system and to develop more complete data on the chemical system. Small-scale continuous-scrubber systems should be built and operated to prove operating capabilities and to study the integrated system in its entirety. If all results are favorable, a pilot plant or small-scale demonstration should complete the program.

SECTION III

INTRODUCTION

BACKGROUND

In the development of sulfur oxide (SO_x) control processes the double-alkali process has emerged as a promising second-generation, regenerable SO_x scrubbing process. Little research and development work has been done on the process and much of what has been done would not apply to the double-alkali process as it is conceived for the U.S. A brief literature study of the process is included as Appendix A.

The double-alkali process involves circulating a clear liquor solution of a soluble alkali salt (Na^+ , K^+ , or NH_4^+) with scrubbing taking place by absorption and reaction to form the bisulfite from the sulfite. The spent scrubbing liquor is then treated with limestone and/or lime to remove solid sulfite (and possibly sulfate) and to regenerate the scrubbing liquor.

Major goals of this program are to regenerate active sodium from the sulfate and to determine methods of controlling steady state sulfate levels in the process. Oxidation and consequent sulfate problems (scaling potential, chemical costs, and water pollution potential) are serious problems in many proposed SO_2 control processes. The double-alkali process appears to have great versatility and should be applicable to both industrial and utility boilers.

REASONS FOR PERFORMING WORK

An experimental program was initiated to study the process chemistry for a double-alkali flow scheme using low concentration (0.01-0.05M) scrubbing solutions of sodium and regeneration using both limestone and lime. It was felt that, although the system appeared promising, there was insufficient data available to warrant a development program without preliminary research. The program planned consists of three phases. Phase I will study the chemistry of both the scrubber and possible regeneration schemes. The bulk of this work will consist of in-house batch reactor experiments designed to study specific reactions and combinations of reactions. Phase II will involve the operation of a small bench-scale scrubber system to study steady state operating modes, oxidation, and solids characteristics. This work will be conducted both in-house and on contract. Phase III will involve the operation of a pilot-scale closed-loop system to characterize feasibility, economics, and operating behavior of the process. The in-house and contract work conducted during the first two phases will support and aid planning of the pilot-plant test program.

APPROACH AND OBJECTIVES

The study discussed here concerns Phase I of the program, the laboratory investigation

of double-alkali regeneration chemistry. Batch tests were carried out in which simulated scrubber effluent solutions were treated with limestone to convert the bisulfite to sulfite. Simulated solutions from this limestone treatment step were then treated with lime to precipitate sulfite and sulfate and return active sodium (NaOH) to the scrubbing

system. The batch tests were carried out under an N_2 purge in a glass vessel submerged in a constant-temperature bath.

The objectives of this work were to study the effects of concentration, stoichiometry, reactant composition, and temperature on reaction rates and reactant utilizations.

SECTION IV

PROCEDURE

PLAN OF INVESTIGATION

An experimental program was carried out to study the chemistry of the scrubber and possible regeneration schemes. The study involved laboratory-scale batch tests for specific reactions and the construction and operation of a bench-scale continuous-scrubber system.

The objectives in carrying out these studies were to generate detailed data on the chemical system of the double-alkali process and to provide an in-house background for the development of a double-alkali process program.

EQUIPMENT

A sketch of the experimental apparatus is shown in Figure 1. Batch reactor experiments were carried out in a 3-liter three-neck flask suspended in a circulating, constant-temperature bath. The reaction vessel was equipped with a variable-speed, propeller-type stirrer, a thermometer, and a nitrogen purge line. Samples were taken through the nitrogen purge port. The purge was necessary to prevent oxidation of the sulfite-bisulfite solutions to sulfate.

The dry calcium carbonate or calcium hydroxide was mixed with roughly half of the water and placed in the reaction vessel. This mixture was stirred and the temperature monitored. The sodium salts were dissolved in the rest of the water and placed in a separate vessel. This vessel was placed in the

constant-temperature bath and the vessel was purged with nitrogen. When both solutions reached the desired temperature, they were poured together in the 3-liter reaction vessel. Mixing of the solution and nitrogen purging of the vessel were maintained throughout the run.

Sampling was carried out by pipetting out 60-70 ml of the mixture and filtering to remove the solids; wet chemical analysis was carried out immediately. Samples were taken from the reaction vessel after 15 or 30 minutes, after 1 hour, and after 3 hours from the time the solutions were poured together.

MATERIALS AND TECHNIQUES

The following reagents were used in the batch experiments:

1. Na_2SO_3 —ACS grade, 98.9% assay, Fisher Scientific (anhydrous).
2. Na_2SO_4 ACS grade, ~99.9% assay, Fisher Scientific.
3. $\text{Na}_2\text{S}_2\text{O}_5$ Analytical reagent, ~97% minimum assay, Mallinckrodt (anhydrite of NaHSO_3).
4. CaCO_3 ACS, 99% minimum assay, Allied Chemical.
ACS, ~99.5% assay, MC&B.
5. $^*\text{Ca}(\text{OH})_2$ Reagent, 93% assay, MC&B.

* Lime mentioned in the text is always hydrated lime or $\text{Ca}(\text{OH})_2$.

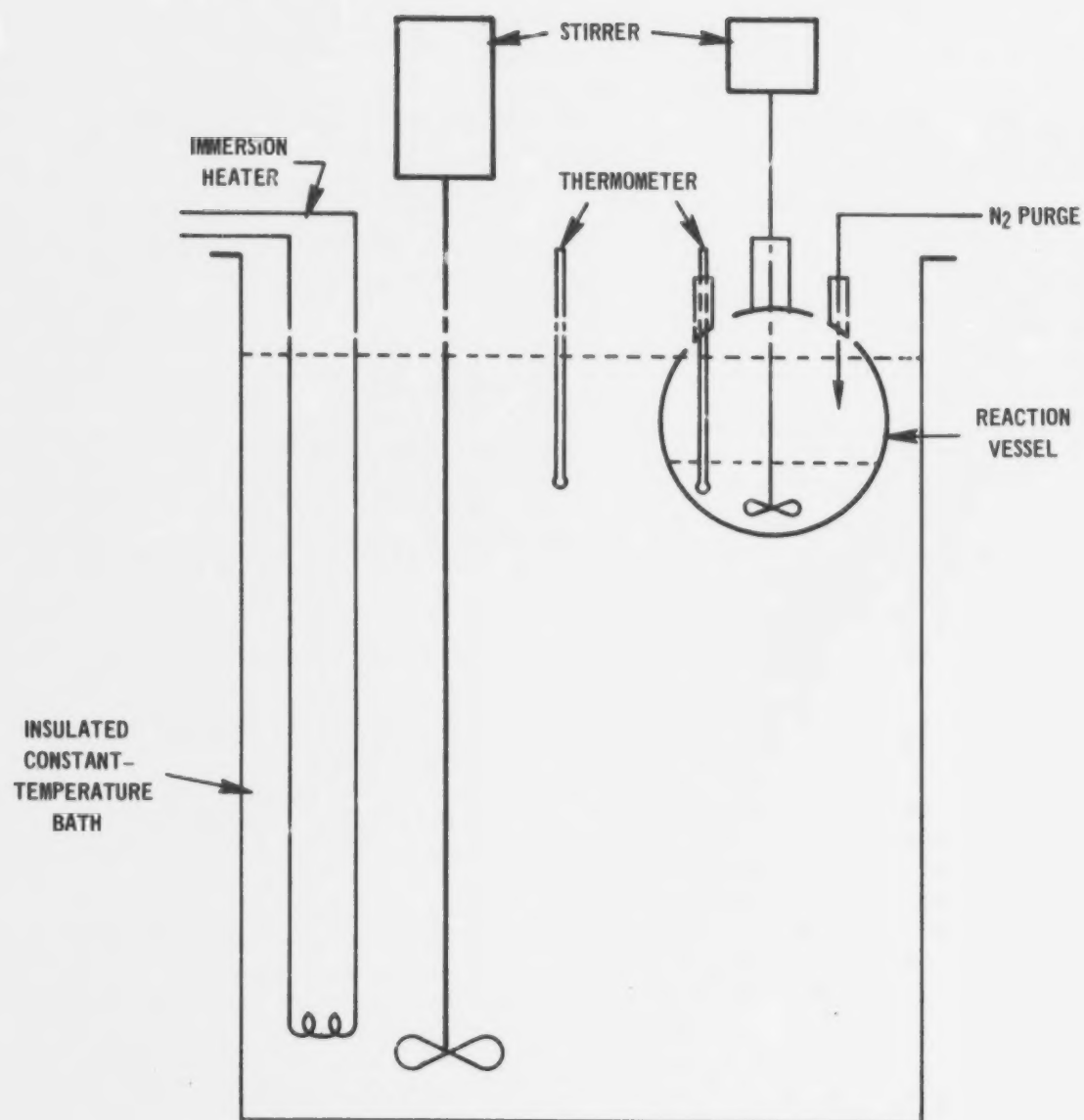


Figure 1. Batch apparatus for studying chemistry of the double-alkali system.

Analytical procedures used for the liquid phase were:

1. Hydroxide—Titrate filtered sample with 0.1N HCl to phenolphthalein endpoint.
2. Sulfite—Add excess of standard 0.1N iodine solution (KI-KIO_3) to sample. Back-titrate the excess iodine with standard 0.05N sodium thiosulfate solution to the starch endpoint.
3. Total Sulfur—Oxidize the sample sulfite species with an amount equal to

the sample volume of 3% hydrogen peroxide. Dilute this solution to 100 ml with distilled water. Treat a portion of this sample with Rexyn 101H resin and let stand for roughly 5 minutes. Titrate a filtered portion of this liquid to a thorin endpoint with $\text{Ba}(\text{ClO}_4)_2$ solution.

4. Calcium—Acidify to dissolve solids (for solids analysis only). Adjust the pH to 12 or 13 with NaOH or KOH. Titrate with EDTA to Eriochrome Blue Black endpoint.

SECTION V

RESULTS AND DISCUSSION

The batch tests were conducted in sets of runs which were planned to study various reactions involved in double-alkali regeneration chemistry. These sets of runs are discussed separately in the following sections.

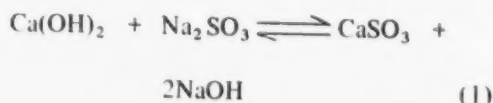
REACTIONS BETWEEN LIME AND SODIUM SULFITE SOLUTIONS

Runs 1-7 were conducted to compare in-house experimental techniques and results with results found by other researchers. The results of these first runs are presented in Table I.

The sulfite levels charged in these experiments correspond to a high sulfur coal. These concentrations are much higher than those proposed for the actual double-alkali scrubber,⁽⁴⁾ but they are the same as those used by

researchers at Arthur D. Little, Inc.⁽⁵⁾ Slightly less lime was charged than would be necessary for complete conversion, but the reaction is equilibrium limited so excess lime is present. The sulfite and hydroxide levels recorded in the table are those analyzed after 1 hour. Run 4 was conducted at 100°F and the rest of the runs at 150°F to check the temperature effect on the rate and equilibrium.

The reaction



has an equilibrium rate constant given by

$$K = \frac{A^2(\text{OH}^-)}{A(\text{SO}_3^{2-})} = \frac{(\gamma_{\text{OH}^-} [\text{OH}^-])^2}{\gamma_{\text{SO}_3^{2-}} [\text{SO}_3^{2-}]}$$

Table 1. BATCH EXPERIMENTS—Ca(OH)₂/Na₂SO₃

Run	Temp °F	Reactants charged, g moles				Analysis g moles/liter (1 hour sample)		$\frac{(\text{OH}^-)^2}{(\text{SO}_3^{2-})}$	
		Ca(OH) ₂	Na ₂ SO ₃	H ₂ O	Additional Additives	OH ⁻	SO ₃ ²⁻	Equilibrium rate constant	Results of others ⁽⁵⁾
1	150	0.466	0.50	50	None	0.81	0.19	3.5	3.4
2	150	0.25	0.25	50	None	0.45	0.053	3.8	4.6
3	150	0.95	1.0	50	None	1.14	0.58	2.2	2.3
4	100	0.25	0.25	50	None	0.44	0.054	3.6	
5	150	0.466	0.50	50	Fe ⁺⁺⁺	0.77	0.18	3.3	
6	150	0.466	0.50	50	Flyash	0.79	0.18	3.5	
7	150	0.466	0.50	50	Fe ⁺⁺⁺ , Flyash	0.85	0.19	3.8	

The activity coefficient, γ , will be concentration dependent. The values for the equilibrium based on concentrations measured will give

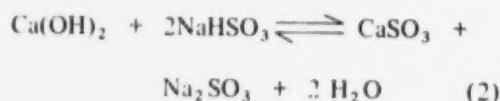
$$\frac{K \gamma_{\text{SO}_3^{2-}}}{\gamma_{\text{OH}^-}^2} = \frac{[\text{OH}^-]^2}{[\text{SO}_3^{2-}]}$$

These values are calculated in Table 1 and compared to the values found by researchers at Arthur D. Little, Inc. The equilibrium values calculated for $[\text{OH}^-]^2/[\text{SO}_3^{2-}]$ agree quite well with values shown in the Arthur D. Little work. The differences may be due to the time required for the completion of the reaction. The Arthur D. Little report stated that the reaction was essentially complete after 1 hour; in-house data indicated only 95 percent completion after 1 hour. The equilibrium values for $[\text{OH}^-]^2/[\text{SO}_3^{2-}]$ calculated after 3 hours of reaction time agree within ± 5 percent of the values found by the Arthur D. Little researchers. The decrease in the equilibrium constant with concentration confirms the Arthur D. Little analysis regarding sulfite ion activity coefficient decrease with concentration increase, and hydroxide ion activity increase with concentration increase. Runs 2 and 4 indicate little, if any, effect from temperature. The concentration effect shown in runs 1, 2, and 3 appears to be significant.

Runs 1, 5, 6, and 7 may be used to determine the effect on the reaction from the presence of corrosion products (Fe^{++}) and/or flyash solubles. As shown in Table 1, values of $[\text{OH}^-]^2/[\text{SO}_3^{2-}]$ for these runs are the same within the experimental error. This "sameness" shows little, if any, effect from either Fe^{++} or flyash solubles on rate or equilibrium concentrations.

REACTIONS BETWEEN LIME AND SULFITE-BISULFITE SOLUTIONS

A second set of runs (45-47) was conducted in which the reactions between lime and both sulfite and bisulfite in the presence of sulfate were studied:



The data for these runs are shown in Table 2. Sufficient lime was charged to convert all of the bisulfite to sulfite and react further with roughly half of the resultant total sulfite. These runs were done at three levels of Na_2SO_4 , corresponding roughly to 5, 10, and 20 wt % solutions. These tests were meant to show the effects of sulfate buildup in the scrubbing solutions on sulfite and bisulfite

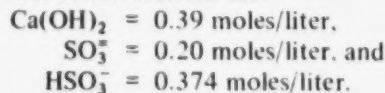
Table 2. BATCH EXPERIMENTS— $\text{Ca(OH)}_2/\text{NaHSO}_3$, Na_2SO_3 , Na_2SO_4
(Runs at 150°F)

Run	Reactants charged, g moles					Analysis, g moles/liter (3-hour sample)		
	Ca(OH)_2	Na_2SO_3	Na_2SO_4	H_2O	NaHSO_3	Total S	OH^-	SO_3^{2-}
45	0.350	0.18	0.35	50	0.34	0.5680	0.3111	0.2424
46	0.360	0.19	0.74	50	0.35	0.9425	0.3770	0.2181
47	0.42	0.22	1.70	50	0.40	1.8298	0.4636	0.2567

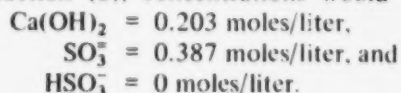
reaction with lime. At these relatively high concentrations, a small effect from ionic strength would be expected. As was mentioned in the previous section, the equilibrium ratio $[\text{OH}^-]^2/[\text{SO}_3^{2-}]$ should be affected by ionic strength, temperature, and reactant concentration. There was, however, insufficient lime present in these runs to allow equilibrium concentrations equivalent to those in Table 1 to be attained. The fractional reaction of the sulfite is roughly the same for all three runs. The slight increases in initial sulfite and hydroxide make these results hard to interpret because of the strong concentration dependence discussed earlier for reaction (1). Additional runs will be conducted and discussed following Table 4. The utilization of lime in the runs shown in Table 2 approached 100 percent as indicated by final SO_3^{2-} and OH^- levels. The utilization was calculated as follows:

The two reactions (1,2) proceed concurrently. The bisulfite neutralization would be expected to go to completion relatively rapidly, considering the rise in pH. Reaction (1) with the sulfite would then proceed to some set of equilibrium concentrations. A sample calculation for run 45 follows to show lime utilization.

Initial concentrations are:



After complete bisulfite conversion by reaction (2), concentrations would be:



The final SO_3^{2-} concentration indicates further reaction between lime and SO_3^{2-} . An additional 0.145 moles/liter of SO_3^{2-} reacts with the Ca(OH)_2 - (intermediate

SO_3^{2-} - final SO_3^{2-}) = (0.387 - 0.242 moles/liter) = 0.145 moles/liter. This would indicate a final OH^- concentration of 0.290 moles/liter by reaction (1). This is in fairly close agreement with the final OH^- concentration measured of 0.311 moles/liter. Overall utilization of Ca(OH)_2 would be:

$$\begin{aligned}& \frac{[\text{Ca(OH)}_2 \text{ for HSO}_3^- + \text{Ca(OH)}_2 \text{ for SO}_3^{2-}]}{[\text{initial Ca(OH)}_2]} \\ &= \frac{[0.187 \text{ moles/liter} + 0.145 \text{ moles/liter}]}{0.390} \\ &= 0.85 \text{ or } 85\% \text{ Ca(OH)}_2 \text{ utilization.}\end{aligned}$$

REACTIONS BETWEEN CALCIUM CARBONATE AND SULFITE-BISULFITE-SULFATE SOLUTIONS

The third set of runs (54-65) was conducted to study the reactions between calcium carbonate and sulfite-bisulfite solutions at different sulfate levels. The emphasis on these runs was to study simulated scrubber solutions with low (less than 0.055M) sulfite and bisulfite concentrations. These low concentrations represent a mode of scrubber operation that appears very promising for future development work.

The results of batch tests 54-65 are shown graphically in Figures 2A, 2B, and 2C, and in Table 3. These tests were conducted to study the reaction between CaCO_3 and simulated scrubber effluent solutions from a dilute scrubber liquor operating mode. CaCO_3 stoichiometries of 1.0 and 1.5 were used. Two sulfite-bisulfite levels were studied at three different sodium sulfate concentrations corresponding roughly to 5, 10, and 20 wt % solutions: Figure 2A is for runs 54-57 with a sodium sulfate level of roughly 5 wt %; Figure 2B

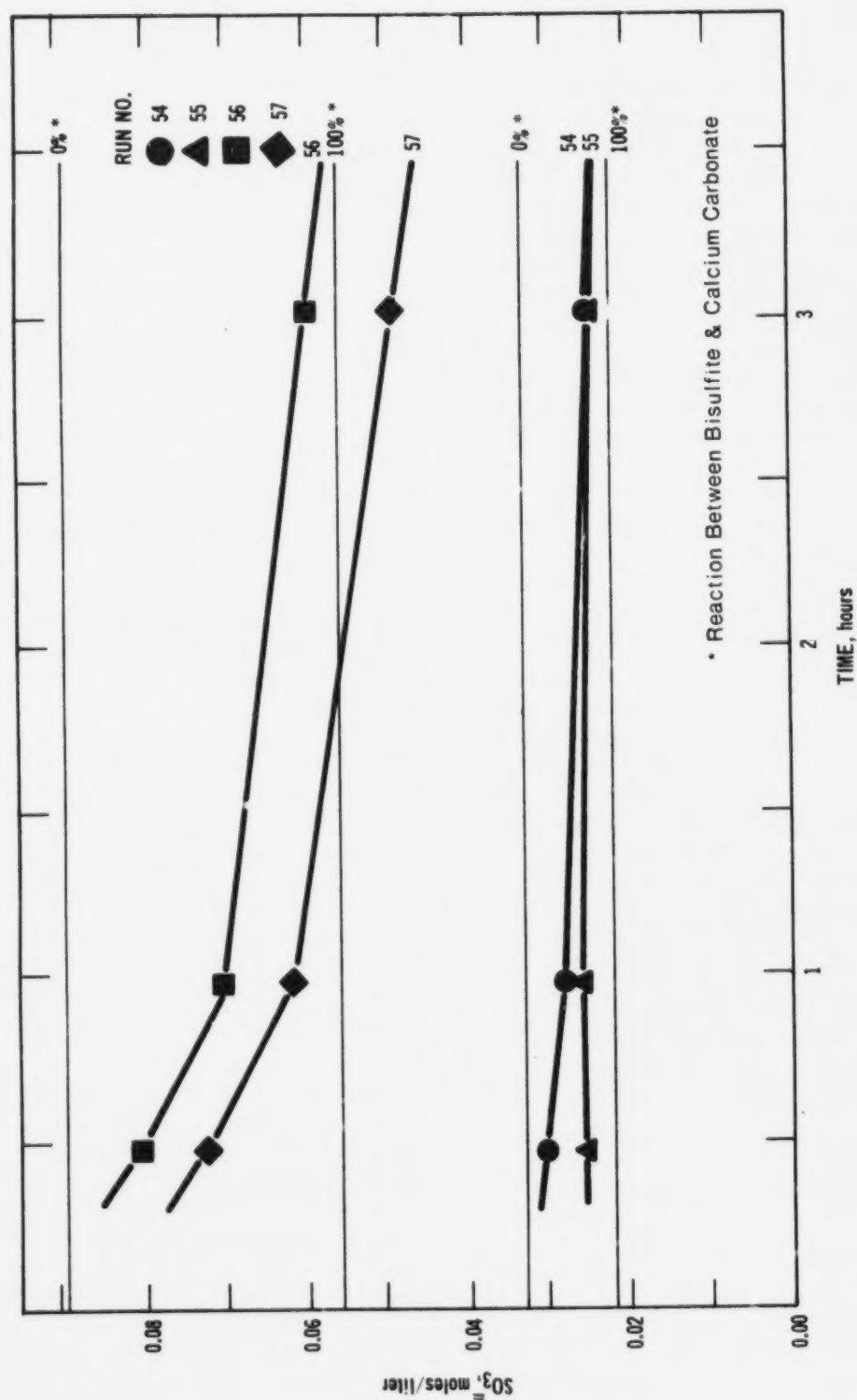


Figure 2A. Runs 54-57 - batch experiments - $\text{CaCO}_3/\text{NaHSO}_3$, Na_2SO_3 , Na_2SO_4 - SO_3^- vs time at ~5 wt % Na_2SO_4 .

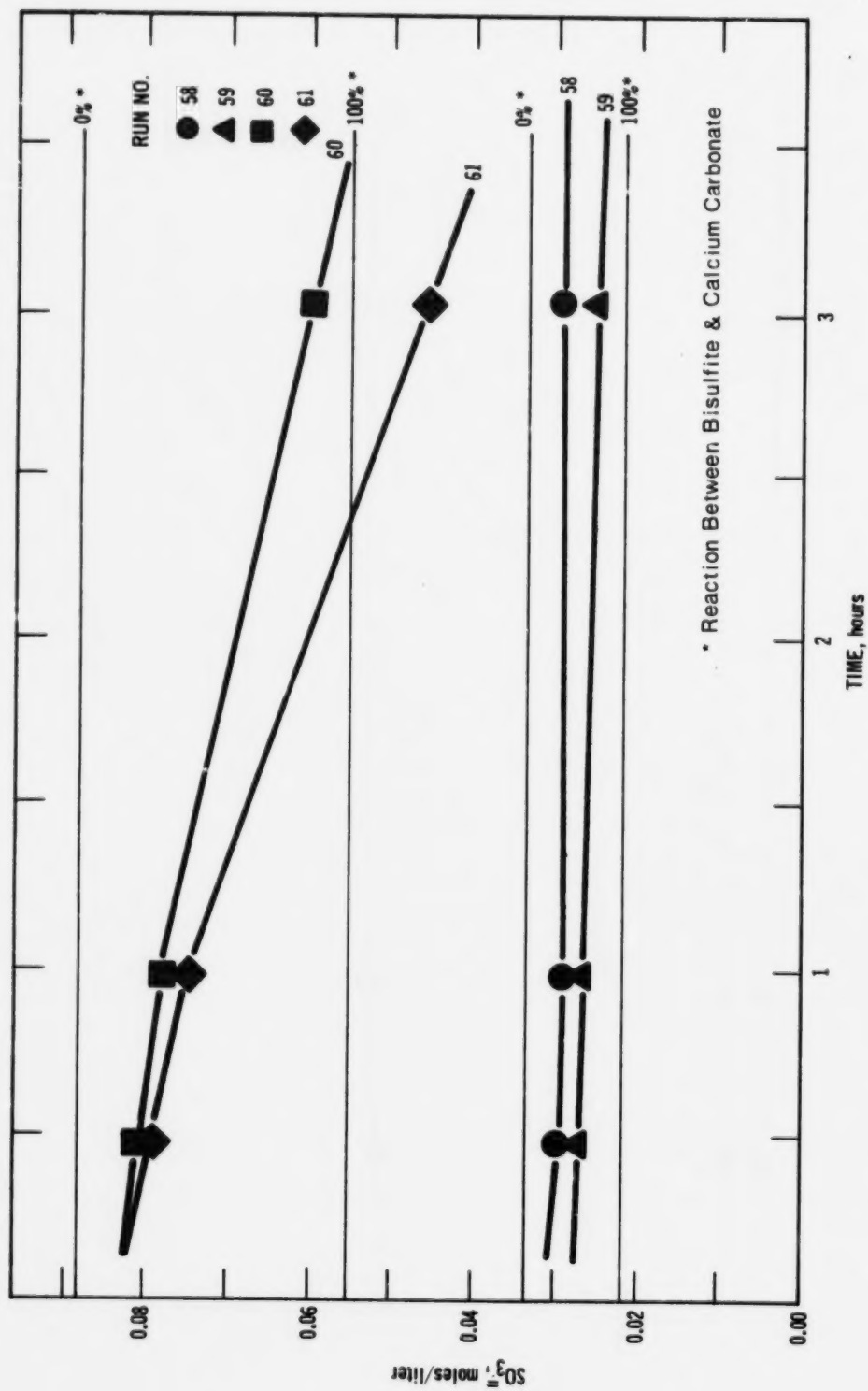


Figure 2B. Runs 58-61 - batch experiments - $\text{CaCO}_3/\text{NaHSO}_3$, Na_2SO_3 , Na_2SO_4 - SO_3^{2-} vs time at $\sim 10 \text{ wt } \% \text{ Na}_2\text{SO}_4$.

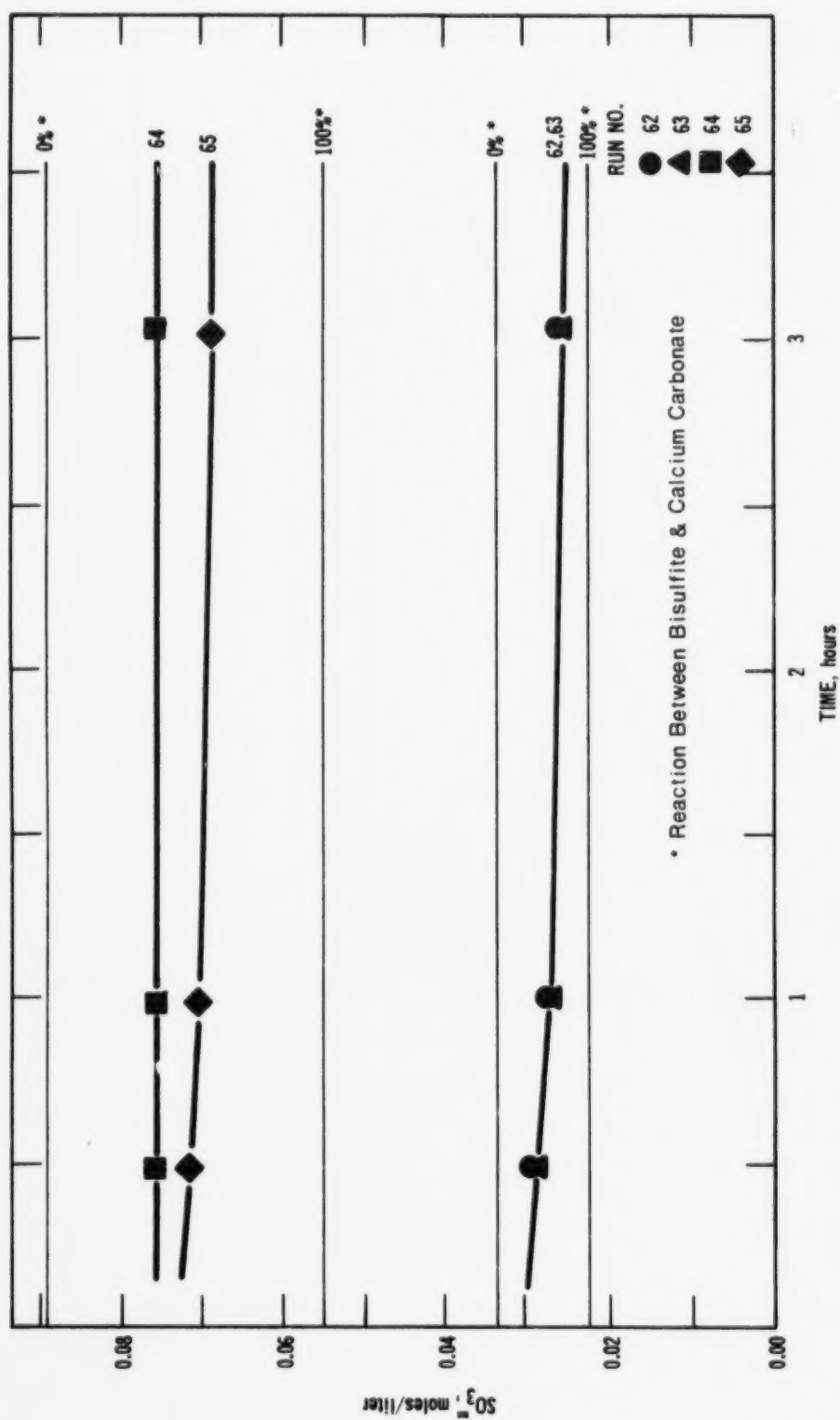
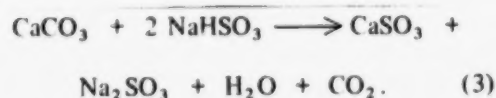


Figure 2C. Runs 62-65 -- batch experiments -- CaCO₃/NaHSO₃, Na₂SO₃, Na₂SO₄ - SO₃²⁻ vs time at ~ 20 wt % Na₂SO₄.

Table 3. BATCH EXPERIMENTS—CaCO₃/NaHSO₃, Na₂SO₃, Na₂SO₄
(All runs at 150°F)

Run	Reactants charged, g moles					SO ₃ ²⁻ analysis, g moles/liter		
	CaCO ₃	Na ₂ SO ₃	NaHSO ₃ as Na ₂ S ₂ O ₅	Na ₂ SO ₄	H ₂ O	1/2 hr	2 hr	3 hr
54	0.01	0.01	0.02	0.33	50	0.0301	0.0273	0.0247
55	0.015	0.01	0.02	0.33	50	0.0311	0.0318	0.0287
56	0.03	0.02	0.06	0.33	50	0.0780	0.0694	0.0580
57	0.045	0.02	0.06	0.33	50	0.0725	0.0605	0.0488
58	0.01	0.01	0.02	0.60	50	0.0297	0.0294	0.0292
59	0.015	0.01	0.02	0.60	50	0.0282	0.0273	0.0254
60	0.03	0.02	0.06	0.60	50	0.0804	0.0782	0.0612
61	0.045	0.02	0.06	0.60	50	0.0811	0.0757	0.0452
62	0.01	0.01	0.02	1.60	50	0.0274	0.0266	0.0259
63	0.015	0.01	0.02	1.60	50	0.0284	0.0269	0.0260
64	0.03	0.02	0.06	1.60	50	0.0756	0.0749	0.0753
65	0.045	0.02	0.06	1.60	50	0.0712	0.0701	0.0676

is for runs 58-61 with a sodium sulfate level of roughly 10 wt %; and Figure 2C is for runs 62-65 with a sodium sulfate level of roughly 20 wt %. The bisulfite conversion reaction is:



The horizontal lines in the figures bracket the range of sulfite concentrations possible corresponding to zero and 100 percent reaction between the bisulfite and the calcium carbonate. As a general trend, the reactions with CaCO₃ stoichiometry of 1.5 proceeded further and faster (lower line in each pair of lines, indicating more complete HSO₃⁻ conversion) than those with stoichiometry of 1.0. With initial bisulfite concentrations of 0.022M, roughly 60 percent reaction occurs after 3 hours at all levels of sulfate. With bisulfite levels of 0.066M it appears that the reaction is suppressed at higher sulfate levels (i.e., less HSO₃⁻ conversion per unit time). Reactant (CaCO₃) utilization (or bisulfite

conversion) at 1.0 stoichiometry ranges from 90-40 percent with increasing sulfate. At 1.5 stoichiometry, bisulfite conversion ranges from 100-64 percent (limestone utilization of 66-40 percent) with increasing sulfate. Additional runs with different sizes of limestone have been conducted and will be discussed later (see Table 9). In general, at a 0.066M bisulfite level greater reactant utilizations are possible than at a 0.022M bisulfite level. This implies a tradeoff between reaction rate, utilization, and sulfite-bisulfite level. Sulfite-bisulfite level in turn affects required liquor rate for a given SO₂ removal and steady state concentrations.

Additional runs were conducted to check reproducibility of this data. A different brand of ACS grade CaCO₃ was used. Better reactant utilization was noted in all runs. Coulter Counter particle size analysis showed the second brand of CaCO₃ to be of finer size. The following paragraph and the Table 9 discussion give more detail.

**Table 4. SPECIAL EXPERIMENTS—STIRRER SPEED EFFECT ON $\text{CaCO}_3/\text{NaHSO}_3$,
 Na_2SO_3 , Na_2SO_4
(All runs at 150°F)**

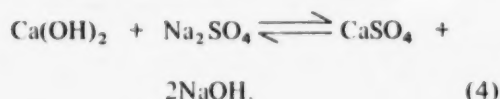
Stirrer speed, rpm	Reactants charged, g moles					$\text{SO}_3^{=}$ analysis, g moles/liter		
	CaCO_3	NaHSO_3	Na_2SO_3	Na_2SO_4	H_2O	1/2 hr	1 hr	3 hr
1300	0.045	0.06	0.02	0.33	50	0.0619	0.0481	0.0388
800	0.045	0.06	0.02	0.33	50	0.0671	0.0517	0.0421
400	0.045	0.06	0.02	0.33	50	0.0660	0.0651	0.0566

Indications are that the reaction is diffusion limited by the CaCO_3 . A check on this hypothesis was made by repeating run 57 at a number of different stirrer speeds. The results of these runs are shown in Table 4. A significant reduction in rate was noted at the reduced stirrer speeds. Lower bisulfite conversions (i.e., higher total sulfite analysis) is noted especially after 1 and 3 hours of reaction time. At the lowest stirrer speed, complete suspension of the solids was not maintained. This would be expected to reduce the extent of the reaction with time. The general trend of reduced rate with reduced stirrer speed is obvious even though slight settling did occur at the lowest agitation level.

REACTIONS BETWEEN CALCIUM HYDROXIDE AND SULFITE-SULFATE SOLUTIONS

Batch tests 66-71 are shown graphically in Figure 3. Table 5 shows the initial charges and results for these runs. These tests were conducted to study the reaction between lime (Ca(OH)_2) and sulfite-sulfate solutions. At both levels of sulfite (0.01M and 0.055M) the highest concentration of Na_2SO_4 appears to suppress OH⁻ formation. Additional information on this reaction can be obtained

from Figure 4 and Table 6. The figure and data are from runs 48-53. The difference between the two sets of runs is: for runs 48-53, an amount of Ca(OH)_2 equivalent to the total sulfate level was used; for runs 66-71, an amount of Ca(OH)_2 equivalent to a 0.15M equilibrium hydroxide concentration was used (from 1/5 to 1/30 the amount in runs 48-53). The results of runs 48-53 show that all the curves for OH⁻ versus time show slightly higher OH⁻ concentrations than the corresponding curves for runs 66-71 and follow the same pattern for OH⁻ formation vs sulfite-sulfate levels. The reaction between Ca(OH)_2 and Na_2SO_4 consists of



A detailed analysis of the data provides an explanation for the somewhat unusual behavior of the OH⁻ vs time curves with respect to initial sulfite-sulfate levels. Table 7 shows some additional calculations for these reactions. The table also shows reactants charged, final $\text{SO}_3^{=}$ and OH⁻, OH⁻ from reaction with $\text{SO}_3^{=}$, and OH⁻ from reaction with $\text{SO}_4^{=}$. It appears that at high sulfate concentrations, sulfite is relatively unreacted after 3 hours. The calculation of OH⁻ from reaction with $\text{SO}_3^{=}$ and OH⁻ from reaction with $\text{SO}_4^{=}$ is done

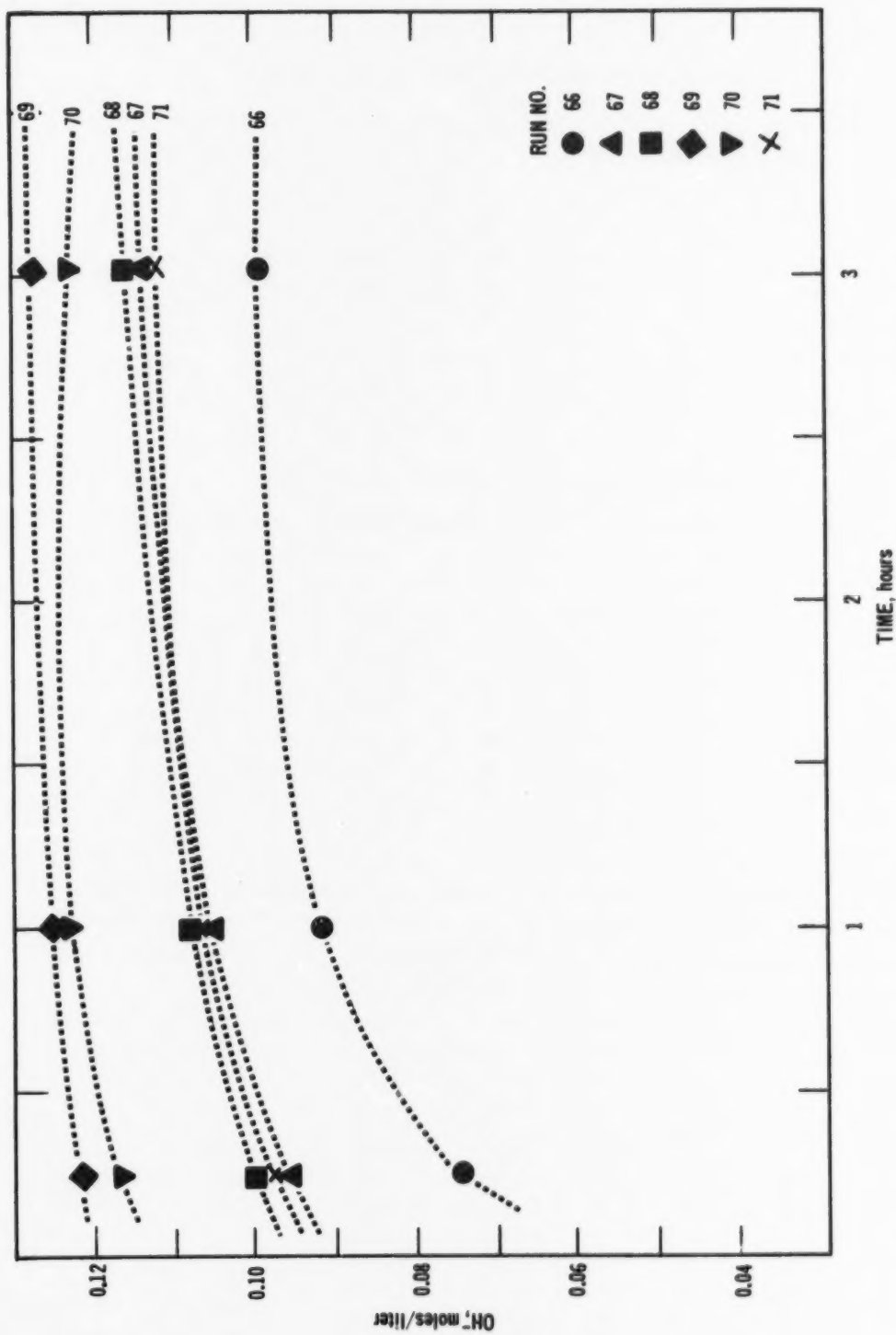


Figure 3. Runs 66-71 - batch experiments - $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4 - \text{OH}^-$ vs time.

Table 5. BATCH EXPERIMENTS— $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4$
(Runs at 150°F)

Run	Reactants charged, g moles				OH ⁻ analysis, g moles/liter		
	Ca(OH)_2	Na_2SO_3	Na_2SO_4	H_2O	1/4 hr	1 hr	3 hr
66	0.07	0.01	0.33	50	0.0750	0.0982	0.1049
67	0.07	0.01	0.60	50	0.1007	0.1086	0.1147
68	0.07	0.01	1.60	50	0.0964	0.1061	0.1159
69	0.07	0.05	0.33	50	0.1214	0.1244	0.1269
70	0.07	0.05	0.60	50	0.1171	0.1232	0.1232
71	0.07	0.05	1.60	50	0.0976	0.1074	0.1135

Table 6. BATCH EXPERIMENTS— $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4$
(Runs at 150°F)

Run	Reactants charged, g moles				OH ⁻ analysis, g moles/liter		
	Ca(OH)_2	Na_2SO_3	Na_2SO_4	H_2O	1/2 hr	1 hr	3 hr
48	0.33	0.01	0.33	50	0.0902	0.1024	0.1037
49	0.70	0.01	0.60	50	0.1251	0.1256	0.1244
50	1.60	0.01	1.60	50	0.1098	0.1171	0.1195
51	0.33	0.05	0.33	50	0.1317	0.1342	0.1366
52	0.70	0.05	0.70	50	0.1348	0.1378	0.1384
53	1.60	0.05	1.60	50	0.1098	0.1195	0.1232

Table 7. BATCH EXPERIMENTS— $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4$ —SUPPLEMENTAL CALCULATIONS

Run	Reactants charged, g moles				Analysis after 3 hours g moles/liter		Calculated OH ⁻ values	
	Ca(OH)_2	Na_2SO_3	Na_2SO_4	H_2O	OH ⁻	$\text{SO}_3^{=}$	From $\text{SO}_3^{=}$	From $\text{SO}_4^{=}$
48	0.33	0.01	0.33	50	0.1037	0.0091	-----	-----
49	0.70	0.01	0.60	50	0.1244	0.0116	-----	-----
50	1.60	0.01	1.60	50	0.1195	0.0116	-----	-----
51	0.33	0.05	0.33	50	0.1366	0.0066	0.0966	0.0400
52	0.70	0.05	0.70	50	0.1384	0.0125	0.0865	0.0519
53	1.60	0.05	1.60	50	0.1232	0.0236	0.0638	0.0594
66	0.07	0.01	0.33	50	0.0927	0.0056	-----	-----
67	0.07	0.01	0.60	50	0.1147	0.0099	-----	-----
68	0.07	0.01	1.60	50	0.1159	0.0079	-----	-----
69	0.07	0.05	0.33	50	0.1269	0.0067	0.0968	0.0301
70	0.07	0.05	0.60	50	0.1232	0.0119	0.0850	0.0382
71	0.07	0.05	1.60	50	0.1135	0.0231	0.0628	0.0507

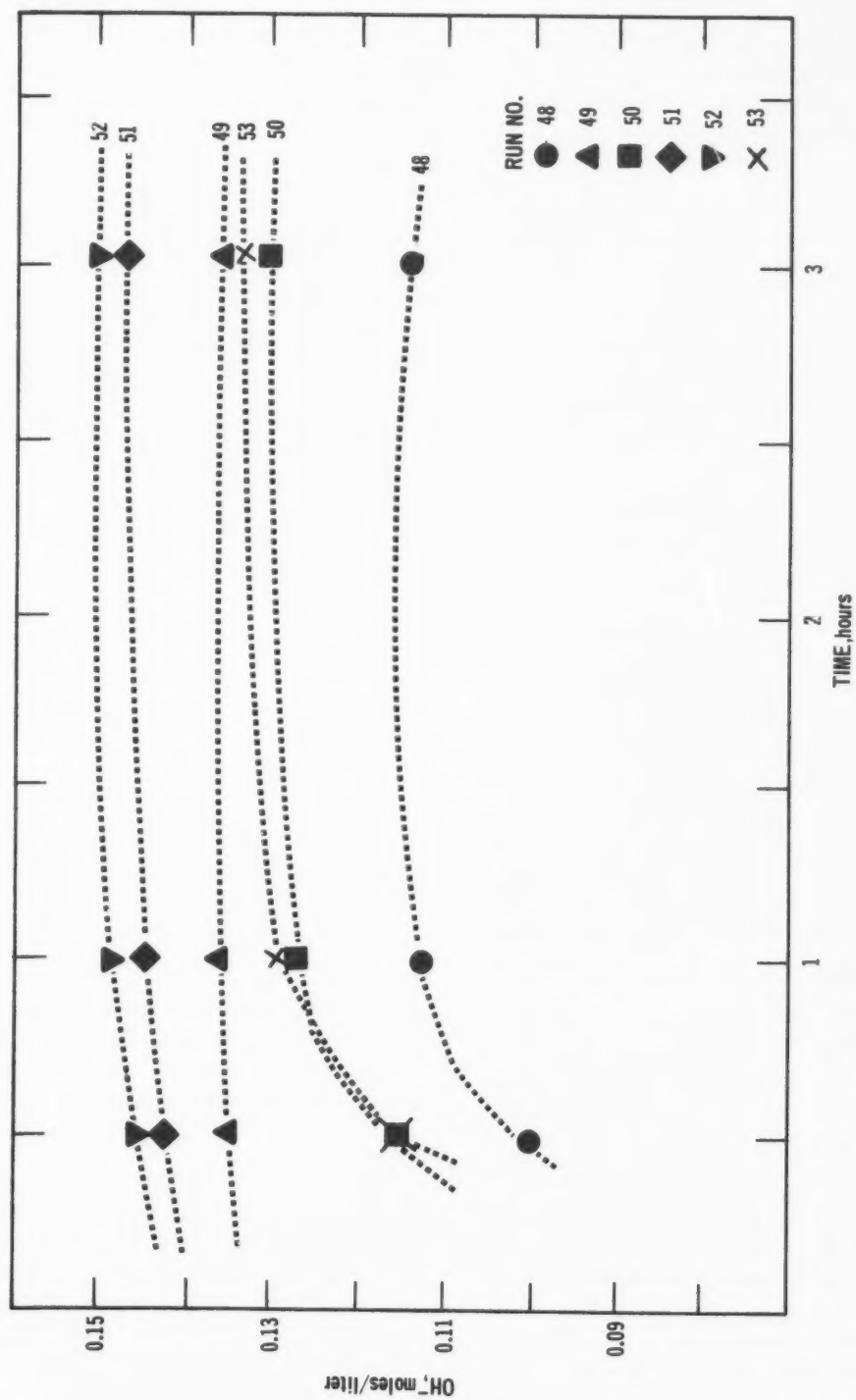


Figure 4. Runs 48-53 — batch experiments — $\text{Ca}(\text{OH})_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4 - \text{OH}^-$ vs time.

only for runs with an initial SO_3^- concentration of 0.055 moles/liter because of the extremely small changes seen in runs with initial SO_3^- concentrations of 0.011 moles/liter.

A sample calculation (using run 69) for OH^- generated from reaction with SO_3^- and from reaction with SO_4^- follows:

Initial concentrations charged were:

$\text{Ca}(\text{OH})_2 = 0.078$ moles/liter,
 $\text{Na}_2\text{SO}_3 = 0.055$ moles/liter, and
 $\text{Na}_2\text{SO}_4 = 0.366$ moles/liter.

Final concentrations measured were:

$\text{OH}^- = 0.1269$ moles/liter, and
 $\text{SO}_3^- = 0.0066$ moles/liter.

Thus, from reaction (1):

$$\begin{aligned}\text{OH}^- &= 2[\text{SO}_3^- \text{ initial} - \text{SO}_3^- \text{ final}] \\ &= 2[0.055 \text{ moles/liter} - 0.0066 \\ &\quad \text{moles/liter}] \\ &= 0.0968 \text{ moles/liter.}\end{aligned}$$

The final OH^- concentration measured was 0.1269 moles/liter. Thus, it can be assumed that the difference between OH^- from reaction (1) and the final OH^- concentration is due to reaction (4). Therefore, the OH^- from reaction (4) is:

$$\begin{aligned}[\text{OH}^- \text{ final} - \text{OH}^- \text{ from reaction (1)}] \\ &= [0.1269 \text{ moles/liter} - 0.0968 \text{ moles/liter}] \\ &= 0.0301 \text{ moles/liter.}\end{aligned}$$

Two effects are obvious. First, as sulfate concentration increases, the reaction with sulfate also increases. Second, as ionic strength (sulfate concentration) increases, the reaction with sulfite is suppressed, as indicated earlier. This result is important in that higher ionic strength (higher SO_4^- levels) favors the reaction of lime with sulfate. The

suppression of the reaction with sulfite may mean that higher sulfite levels may be used in a scrubber without precluding the regeneration of inactive Na_2SO_4 to active NaOH by the use of lime.

One additional fact should be noted from Table 7. Comparing runs 51-53 and 69-71 indicates that increased $\text{Ca}(\text{OH})_2$ to Na_2SO_3 stoichiometry does not affect the amount of SO_3^- reacted (OH^- from SO_3^-). Increasing $\text{Ca}(\text{OH})_2$ to Na_2SO_4 stoichiometry significantly changes the amount of SO_4^- reacted (OH^- from SO_4^-). This effect can be seen by noting the similarities in the values of OH^- from SO_3^- for runs 51-53 and 69-71 and the differences in the OH^- from SO_4^- values between these same sets of runs.

The OH^- levels observed imply at least some reaction with sulfate. Total sulfur measurement did not give usable results. Arthur D. Little, Inc. had similar difficulty in some of its work.

The following section discusses two additional runs and supports implications from the data on runs 66-71 and 48-53.

REACTIONS BETWEEN CALCIUM HYDROXIDE AND SULFITE-SULFATE SOLUTIONS—CHECKS ON ANALYTICAL RESULTS AND IMPLICATIONS

Two additional runs were made: one as a blank on sulfite; the other as a blank on both sulfite and sulfate. These runs were conducted to show the accuracy of the experimental methods and to support the implications given by the data discussed following Table 4. Table 8 lists reactants charged and analytical results for these runs (72 and 73) along with two previously discussed regular runs (67

Table 8. BATCH EXPERIMENTS — $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3, \text{Na}_2\text{SO}_4$ — CHECKS ON ANALYTICAL RESULTS AND IMPLICATIONS
(Runs at 150°F)

Run	Reactants charged, g moles				$\text{SO}_3^{=}$ analysis g moles/liter			OH^- analysis g moles/liter		
	Ca(OH)_2	Na_2SO_3	Na_2SO_4	H_2O	1/4 hr	1 hr	3 hr	1/4 hr	1 hr	3 hr
67	0.07	0.01	0.60	50	0.0103	0.0103	0.0103	0.1028	0.1080	0.1110
70	0.07	0.05	0.06	50	0.0165	0.0131	0.0122	0.1190	0.1241	0.1248
72	0.07	—	—	50	0.0008	0.0006	0.0006	0.0317	0.0323	0.0305
73	0.07	—	0.60	50	0.0016	0.0016	0.0016	0.1086	0.1086	0.1116

and 70). Figures 5 and 6 show the analysis for $\text{SO}_3^{=}$ and OH^- , respectively, as a function of time for these runs (67, 70, 72, and 73). The lowest line in Figure 6 shows a hydroxide ion background level corresponding to the equilibrium dissolution of calcium hydroxide when no sulfite or sulfate is present for reaction. The lower two lines in Figure 5 show the background $\text{SO}_3^{=}$ level in the presence of sulfate only and with neither sulfite nor sulfate present. From the measured OH^- and $\text{SO}_3^{=}$ levels in the blank runs (72 and 73) and the measured OH^- and $\text{SO}_3^{=}$ levels in the two regular runs (67 and 70) used for comparison, it is inferred that from 25 to 72 percent of the calcium hydroxide is reacted with the sulfate in the presence of these low sulfite concentrations. The amount reacted depends on both initial sulfite-sulfate ratio and concentration. A sample calculation showing the rationality of this inference is given below.

Comparing runs 72 and 73 shows an equilibrium OH^- concentration corresponding to the solubility of Ca(OH)_2 in run 72 versus the reaction of $\frac{0.1116}{2}$ moles/liter of Ca(OH)_2 (by reaction (4)) with the sulfate in run 73. Run 70 shows a 3-hour OH^- concentration appreciably higher than for run 73 where no sulfite

was present. There are two competing reactions in run 70 (1,4). The change in sulfite generates 0.0856 moles/liter of hydroxide.

$$2[\text{SO}_3^{=} \text{ initial} - \text{SO}_3^{=} \text{ final}]$$

$$= 2[0.055 \text{ moles/liter} - 0.0122 \text{ moles/liter}]$$

$$= 0.0856 \text{ moles/liter OH}^-$$

The final hydroxide ion concentration in run 70 of 0.1248 moles/liter implies an additional reaction of lime with sulfate.

$$[\text{OH}^- \text{ final} - \text{OH}^- \text{ from sulfite reaction}]$$

$$= [0.1248 \text{ moles/liter}$$

$$- 0.0856 \text{ moles/liter}]$$

$$= 0.0392 \text{ moles/liter OH}^-$$

Thus, the fraction of the lime which reacts with the sulfate is

$$\frac{\text{lime reacted with sulfate}}{\text{total initial lime}}$$

$$= \frac{0.0392 \text{ moles/liter}}{0.077 \text{ moles/liter}} = 25.4\%$$

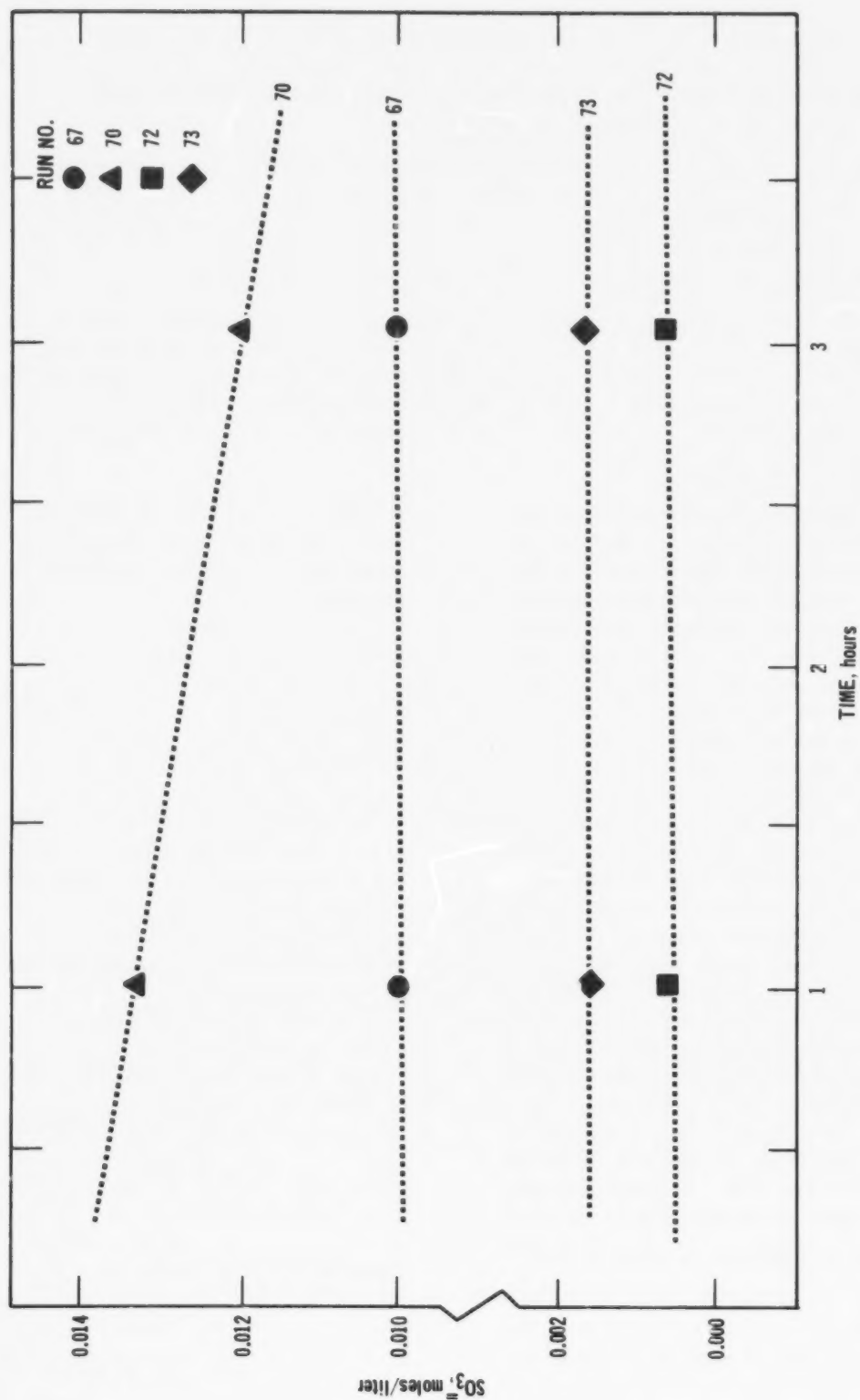


Figure 5. Runs 67, 70, 72, 73 — special experiments — $\text{Ca(OH)}_2/\text{Na}_2\text{SO}_3$, Na_2SO_4 — checks on analytical results — SO_3^- vs time.

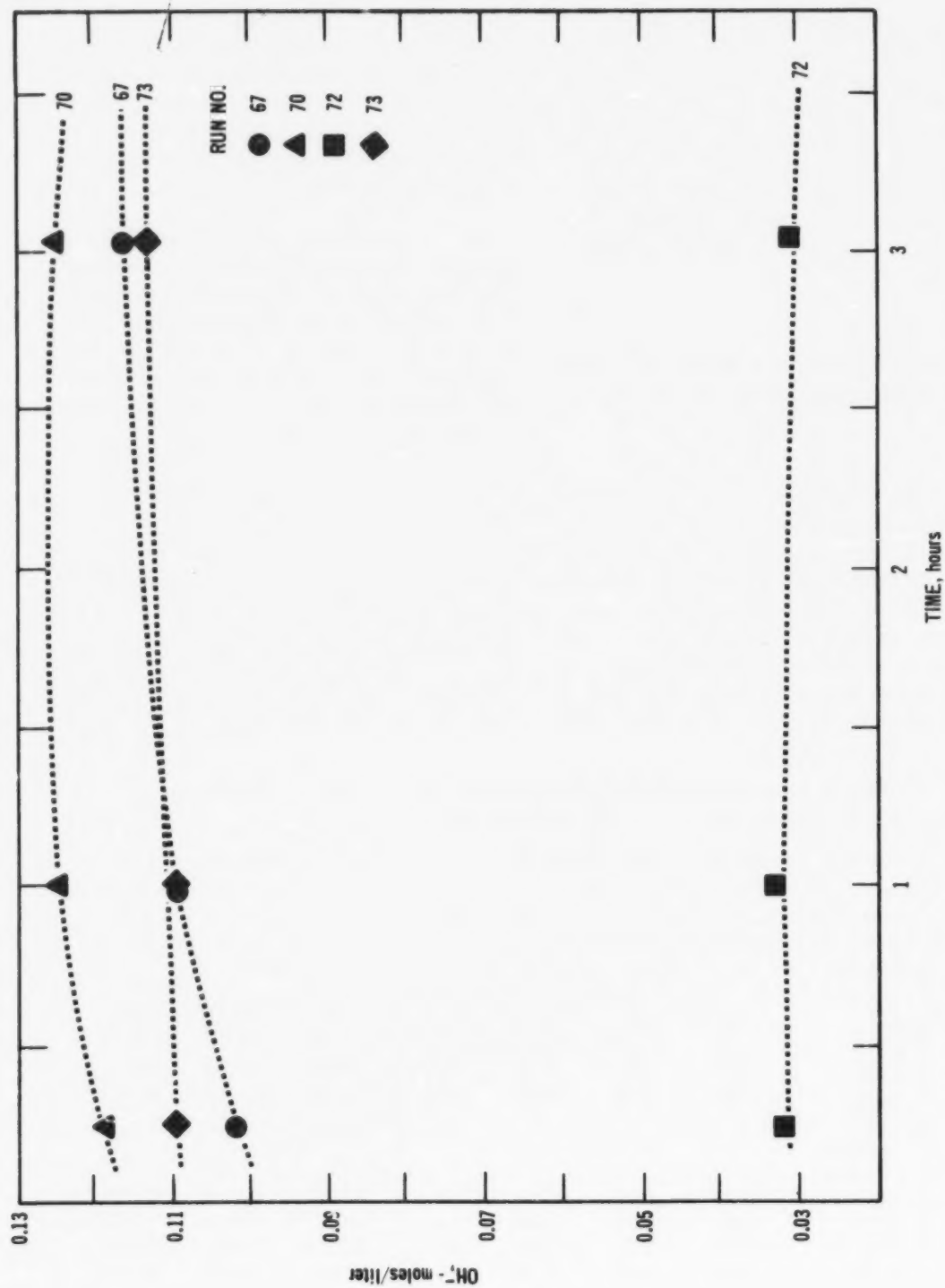


Figure 6. Runs 67, 70, 72, 73 — special experiments — $\text{Ca}(\text{OH})_2/\text{Na}_2\text{SO}_3 \cdot \text{Na}_2\text{SO}_4$ — checks on analytical results — OH^- vs time.

The same reasoning can be applied to runs 66-71 and 48-53 to show that, in the presence of the low sulfite levels studied, significant reaction of the calcium hydroxide with sulfate does occur. Overall utilizations of calcium hydroxide with the simulated scrubber solutions (runs 66-71) amounted to 69-83 percent after 3 hours of reaction time.

REACTIONS BETWEEN LIMESTONE AND SULFITE-BISULFITE-SULFATE SOLUTIONS

Runs were conducted with two grinds of Fredonia limestone (representing the stones being used at the Shawnee wet limestone test facility) to compare the effect of particle size on bisulfite neutralization with limestone. The two grinds, "Fredonia fine" and "Fredonia coarse," were processed through an 18-mesh screen to remove lumps. The particle size distribution of these two stones was

determined by Coulter Counter analysis. The Coulter Counter results indicate that the "Fredonia fine" stone was 50 percent by mass less than 6μ , and 90 percent by mass less than 22μ . The "Fredonia coarse" stone was 50 percent by mass less than 12μ , and 90 percent by mass less than 45μ .

Table 9 lists the reactants charged and the resultant total sulfite concentrations analyzed as a function of time. Runs were conducted at a sulfate level corresponding to roughly 10 wt % Na_2SO_4 in solution. Two bisulfite concentrations (0.02 and 0.06 g moles charged) were studied for each stone with limestone stoichiometries of 1.0 and 1.5.

Three-hour total sulfite levels indicate slightly higher reaction rates with the finer stone. Differences might be considered almost insignificant, although the small magnitude of the difference in size of the two stones is probably responsible for the slight differences in reaction rates. Results shown in Table 4, indicating the effect of stirrer speed, imply that the reaction is diffusion limited by the

Table 9. BATCH EXPERIMENTS - LIMESTONES/ NaHSO_3 , Na_2SO_3 , Na_2SO_4

Run	Reactants charged, g moles					Total SO_3^{2-} analysis g moles/liter		
	CaCO_3	NaHSO_3	Na_2SO_3	Na_2SO_4	H_2O	1/2 hr	1 hr	3 hr
	Fredonia fine							
74	0.01	0.02	0.01	0.60	50	0.0188	0.0158	0.0116
75	0.015	0.02	0.01	0.60	50	0.0174	0.0165	0.0123
76	0.03	0.06	0.02	0.60	50	0.0548	0.0441	0.0402
77	0.045	0.06	0.02	0.60	50	0.0562	0.0412	0.0403
	Fredonia coarse							
78	0.01	0.02	0.01	0.60	50	0.0177	0.0138	0.0185
79	0.015	0.02	0.01	0.60	50	0.0127	0.0116	0.0130
80	0.03	0.06	0.02	0.60	50	0.0562	0.0487	0.0443
81	0.045	0.06	0.02	0.60	50	0.0547	0.0446	0.0405

CaCO_3 . The slightly increased rate with the finer limestone supports this implication. Very fine and very coarse ($\sim 10\mu$ vs 100μ) stones should be compared to amplify the slight differences seen in these runs. The rates and utilizations of reactants using natural limestone compare favorably with those using reagent grade CaCO_3 .

CALCIUM ION CONCENTRATIONS IN SCRUBBER SOLUTIONS

Calcium ion concentrations in related scrubber solutions are of prime importance to this study. A number of calcium ion deter-

minations were done but, by themselves, were felt to have little value. The most revealing method of studying Ca^{++} concentrations and related SO_3^- and SO_4^- concentrations is to operate a small-scale continuous-scrubber system and measure concentrations of interest at steady state conditions. A followup to the batch tests reported in this study will consist of runs on a small, continuous double-alkali scrubber. Actual operating conditions will be closely simulated and steady state concentrations will be determined for the important components of the scrubber solutions. Special attention will be given to Ca^{++} , SO_3^- , and SO_4^- concentrations at various points of interest in the scrubber loop.

SECTION VI

ACKNOWLEDGEMENTS

Assistance is gratefully acknowledged to J. H. Abbott for his counsel and advice throughout, along with many reviews of the material generated. Thanks and credit are also due to J. W. Rives and B. E. Daniel for much

time spent in conscientious effort on the experimental work and to R. E. Valentine for assistance in preparing this report. All are members of this Division's Research Laboratory Branch.

SECTION VII APPENDICES

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APPENDIX A

DOUBLE-ALKALI PROCESS LITERATURE STUDY AND REFERENCES

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Appendix B. EXPERIMENTAL DATA AND RESULTS
(All runs at 150°F unless otherwise noted)

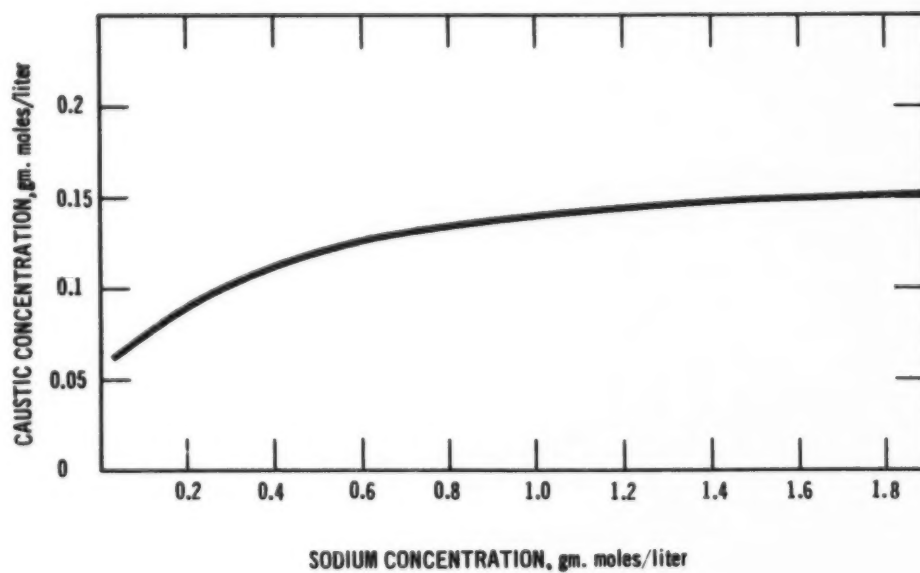
Run	Reactants charged, g moles						SO ₃ analysis g moles/liter			OH ⁻ analysis g moles/liter			
	Ca(OH) ₂	CaCO ₃	Na ₂ SO ₃	NaHSO ₃	Na ₂ SO ₄	H ₂ O	Other	1/2 hr	1 hr	3 hr	1/2 hr	1 hr	3 hr
1	0.466		0.50			50		0.1935	0.1875	0.1865	0.7978	0.8125	0.8175
2	0.25		0.25			50		0.0508	0.0535	0.0494	0.4431	0.4480	0.4634
3	0.95		1.0			50		0.5792	0.5861	0.5924	1.125	1.141	1.169
4*	0.25		0.25			50		0.5900	0.0543	0.0535	0.4278	0.4382	0.4452
5	0.466		0.50			50	Fe ⁺⁺⁺	0.1776	0.1769	0.1653	0.7728	0.7978	0.8052
6	0.466		0.50			50	Flyash	0.1832	0.1797	0.1852	0.7686	0.7905	0.8064
7	0.466		0.50			50	Fe ⁺⁺⁺ , Fly- ash	0.2081	0.1922	0.1685	0.8723	0.8466	0.7820
45	0.35		0.18	0.34	0.35	50		0.2587	0.2537	0.2424	0.2933	0.2989	0.3111
46	0.36		0.19	0.35	0.74	50		0.2344	0.2256	0.2181	0.3721	0.3721	0.3770
47	0.42		0.22	0.40	1.70	50		0.2535	0.2642	0.2567	0.4331	0.4514	0.4636
48	0.33		0.01		0.33	50		0.0153	0.0096	0.0091	0.0902	0.1024	0.1037
49	0.70		0.01		0.60	50		0.0111	0.0106	0.0116	0.1251	0.1256	0.1244
50	1.60		0.01		1.60	50		0.0106	0.0116	0.0116	0.1098	0.1171	0.1195
51	0.33		0.05		0.33	50		0.0076	0.0076	0.0066	0.1317	0.1342	0.1366
52	0.70		0.05		0.70	50		0.0179	0.0178	0.0125	0.1348	0.1378	0.1384
53	1.60		0.05		1.60	50		0.0384	0.0327	0.0236	0.1098	0.1195	0.1232
54		0.01	0.01	0.02	0.33	50		0.0301	0.0273	0.0247			
55		0.015	0.01	0.02	0.33	50		0.0311	0.0318	0.0287			
56		0.03	0.02	0.06	0.33	50		0.0780	0.0694	0.0580			
57		0.045	0.02	0.06	0.33	50		0.0725	0.0605	0.0488			
57-2		0.045	0.02	0.06	0.33	50	400 rpm	0.0660	0.0651	0.0566			
57-3		0.045	0.02	0.06	0.33	50	800 rpm	0.0671	0.0517	0.0421			
57-4		0.045	0.02	0.06	0.33	50	1300 rpm	0.0619	0.0481	0.0388			
58		0.01	0.01	0.02	0.60	50		0.0297	0.0294	0.0292			
59		0.015	0.01	0.02	0.60	50		0.0282	0.0273	0.0254			
60		0.03	0.02	0.06	0.60	50		0.0804	0.0782	0.0612			
61		0.045	0.02	0.06	0.60	50		0.0811	0.0757	0.0452			
62		0.01	0.01	0.02	1.60	50		0.0274	0.0266	0.0259			
63		0.015	0.01	0.02	1.60	50		0.0284	0.0269	0.0260			
64		0.03	0.02	0.06	1.60	50		0.0756	0.0749	0.0753			
65		0.045	0.02	0.06	1.60	50		0.0712	0.0701	0.0676			

Appendix B (Cont'd). EXPERIMENTAL DATA AND RESULTS

Run	Reactants charged, g moles						SO ₃ analysis g moles/liter				OH ⁻ analysis g moles/liter		
	Ca(OH) ₂	CaCO ₃	Na ₂ SO ₃	NaHSO ₃	Na ₂ SO ₄	H ₂ O	1/4 hr	1/2 hr	1 hr	3 hr	1/2 hr	1 hr	3 hr
66	0.07		0.01		0.33	50	0.006		0.006	0.0056	0.0750	0.0982	0.1049
67	0.07		0.01		0.60	50			0.0099	0.0099	0.1007	0.1086	0.1147
68	0.07		0.01		1.60	50			0.0093	0.0079	0.0964	0.1061	0.1159
69	0.07		0.05		0.33	50			0.0096	0.0067	0.1214	0.1244	0.1269
70	0.07		0.05		0.60	50			0.1320	0.1190	0.1171	0.1232	0.1232
71	0.07		0.05		1.60	50	0.0454		0.0311	0.0231	0.0976	0.1074	0.1135
72	0.07					50	0.0008		0.0006	0.0006	0.0317	0.0323	0.0305
73	0.07				0.60	50	0.0016		0.0016	0.0016	0.1086	0.1086	0.1116
Fredonia fine													
74		0.01	0.01	0.02	0.60	50		0.0188	0.0158	0.0116			
75		0.015	0.01	0.02	0.60	50		0.0174	0.0165	0.0123			
76		0.03	0.02	0.06	0.60	50		0.0548	0.0441	0.0402			
77		0.045	0.02	0.06	0.60	50		0.0562	0.0412	0.0403			
Fredonia coarse													
78		0.01	0.01	0.02	0.60	50		0.0177	0.0138	0.0185			
79		0.015	0.01	0.02	0.60	50		0.0127	0.0116	0.0130			
80		0.03	0.02	0.06	0.60	50		0.0562	0.0487	0.0443			
81		0.045	0.02	0.06	0.60	50		0.0547	0.0446	0.0405			

*Run at 100° F

APPENDIX C
EQUILIBRIUM CAUSTIC FORMATION
IN $\text{Ca}(\text{OH})_2$ - Na_2SO_4 SOLUTIONS^a
(at 120°F)



^aReproduced from reference 7.